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PATENT ABSTRACTS OF JAPAN

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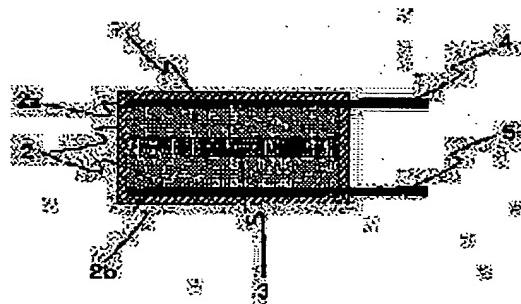
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(54) LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent decrease in electric current density due to low conductivity of lithium ions in the electrolyte, and for example, to eliminate the need for containing organic solvent or lithium salt, which is a lithium ion conductor in an electrolyte.

SOLUTION: This lithium battery holding solid electrolyte layer lies between a pair of electrodes. The electrode and the solid electrolyte layer contain a compound made of siloxane bond and a non-protonic solvent as a main structure.



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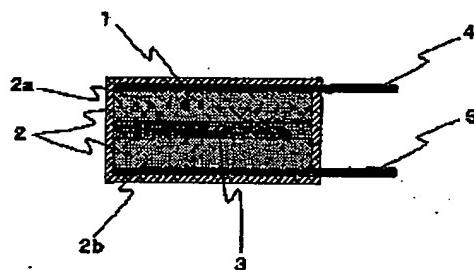
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(54)【発明の名称】 リチウム電池

(57)【要約】

【課題】 電解質のリチウムイオン伝導度が低くて電流密度が小さく、例えばリチウムイオン伝導体である有機溶媒やリチウム塩を電解質に含ませる必要があるという問題があった。

【解決手段】 一対の電極間に固体電解質層を挟持してなるリチウム電池であって、前記電極および固体電解質層がシロキサン結合を主骨格とする化合物と非プロトン性溶媒を含んでいることを特徴とする。



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【特許請求の範囲】

【請求項1】 一対の電極間に固体電解質層を挟持してなるリチウム電池であって、前記電極および固体電解質層がシリコキサン結合(Si-O)を主骨格とする化合物と非プロトン性溶媒を含んでいることを特徴とするリチウム電池。

【請求項2】 前記電極が電極活性物質と固体電解質から成り、前記固体電解質層がこの固体電解質と同一材料から成ることを特徴とする請求項1に記載のリチウム電池。

【請求項3】 前記固体電解質層がリチウムイオン伝導性を有する酸化物系結晶化ガラスから成ることを特徴とする請求項1または請求項2に記載のリチウム電池。

【請求項4】 前記非プロトン性溶媒が、アーブチロラクトン、プロピレンカーボネート、エチレンカーボネートのいずれか一種または複数種から成ることを特徴とする請求項1、請求項2または請求項3に記載のリチウム電池。

【請求項5】 前記電極の活性物質がLi_xMn_{1-x}O_y(0≤x≤0.2)、LiMn_{1-y}Me_yO_z(Me=N_{1-x}Cr_x、Cu、Zn, 0<y≤0.6)、Li_xTi_{1-x}O₂、およびLi_xMn_{1-x}O₂のいずれか一種または複数種からなることを特徴とする請求項1、請求項2、請求項3または請求項4に記載のリチウム電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明はリチウム電池に関するものである。

【0002】

【従来の技術および発明が解決しようとする課題】 リチウム電池はエネルギー密度が高く、自己放電が少なく、長期保存に対応できるなどの特性を生かし、携帯電話やノートパソコンなどに広く用いられている。これらリチウム電池は、正極活性物質としてコバルト酸リチウム(LiCoO₂)やマンガン酸リチウム(LiMn₂O₄)が一般的に用いられ、負極活性物質には、コーカスや炭素繊維などの炭素材料が用いられている。

【0003】 一般的にリチウム電池は、前述の正極活性物質や負極活性物質とアセチレンブラックや黒鉛などの導電剤とポリフッ化ビニリデン(PVdF)やポリテトラフルオロエチレン(PTFE)などの結着剤と共にアルミ箔もしくは銅箔に塗付され、ポリプロピレン製またはポリエチレン製もしくはそれらの組み合わせであるセパレータを介してスパイラル状に巻き取られて電池缶内に挿入され、さらに有機系電解液を注入して封口された構造になっている。

【0004】 これら有機系電解液の構成要素は非プロトン性溶媒と電解質塩であり、非プロトン性溶媒としてはプロピレンカーボネート(PC)、ジメトキシエタン(DME)、エチレンカーボネート(EC)、ジメチル

カーボネート(DMC)、ジエチルカーボネート(DEC)が単独あるいは混合された状態で用いられ、電解質塩としてはLiClO₄、LiAsF₆、LiBF₄、LiPF₆、LiCF₃SO₃、Li(CF₃SO₃)₂Nなどが用いられている。

【0005】 また、近年、携帯電話やノートパソコンなどの携帯用情報通信端末に代表される各種電子応用機器の薄型かつ小型化の要求に伴い、前述のような有機系電解液に代えて、ポリマー電解質を用いたリチウム電池が注目されている。

【0006】 ポリマー電解質は、ポリエチレンオキシド(PEO)やポリプロピレンオキシド(PPG)に代表されるドナー型の極性基を有する高分子と電解質塩との混合剤であり、電解質層を薄膜化することができエネルギー密度の向上が期待される。あるいは、漏液、腐食の心配がなく、揮発性の非プロトン性溶媒を用いないため、爆発や発火の危険性が少ないなど、電池特性や安全性の向上が望める。

【0007】 しかしながら、前述のポリマー電解質は、有機系電解液と比較してイオン導通度が低いという問題があり、ポリマー電解質に有機系電解液を混合したゲル電解質は、有機系電解液に匹敵するイオン導通度を有することから、開発が盛んに行われている。

【0008】 このようなゲル電解質を用いた場合、固体電解質層と電極層の電気的な接觸を理想的に保つことが困難であり、例えば特開平7-326383号公報では、高分子化合物に電解質塩と溶媒を混合してモノマー組成物を重合させたものを正極活性物質層に積層してモノマー組成物の一部を正極活性物質層に含浸させ、正極活性物質層に含浸させたモノマー組成物と正極活性物質の表面に積層したモノマー組成物を重合して正極活性物質層に密着して高分子固体電解質を積層状態に作製することによって正極活性物質層と高分子固体電解質とを十分に密着させることができると提案されている。

【0009】 また、特開平8-111233号公報では、正極酸化物表面にポリエーテル、ポリチオエーテル、またはポリアクリレートの主鎖の両端または一端が化学結合した正極と固体電解質との界面の抵抗、および正極活性物質粒子同士の界面抵抗を低減させることができると提案されている。

【0010】 また、特開平8-315855号公報では、重合可能な官能基を有する有機化合物と有機溶媒とリチウム塩との混合物を両電極間に挟み、その後に重合を完結させることにより、電解質と電極との間ににおける界面の生成を防止し、固体電解質と電極との影響を防ぐことなどが提案されている。

【0011】 また、特開平9-50816号公報では、溶質と電解質塩を混合させた高分子電解質中に、Li₂CO₃、CoCO₃、NiCO₃、MgCO₃などの金属炭酸物を分散させることにより、機械的性質や加工性に

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優れるとともに、負極との界面における化学的安定性の高い複合固体電解質が提案されている。

【0012】しかしながら、これらの方法では依然として電解質のリチウムイオン伝導度が低く電流密度が小さくなってしまう問題があり、主たるリチウムイオン伝導体である有機溶媒およびリチウム塩を多く含ませる必要があった。また、有機溶媒にリチウム塩を含ませることにより、電気化学反応に対する耐電圧が低くなる問題があり、過電圧に対して不安定であるという問題がある。

【0013】さらには、固体電解質に無機化合物を用いた固体電解質電池の開発も進められている。正極活物質として遷移金属酸化物および遷移金属硫化物からなる化合物を正極とし、Li_xSを含むリチウムイオン伝導性的ガラス固体電解質およびリチウムと合金化する金属を負極とする全固体リチウム電池で負極におけるデンドライドの発生や活物質の脱落がなく、充放電サイクル寿命に優ることが提案されている。ただし、この提案は、正極および固体電解質に硫化物系の化合物を含むため、水分との反応性に富むなどの問題がある。

【0014】また、酸化物系のリチウムイオン伝導体では、NASICON系と同様の結晶構造を有する結晶質ガラスがあり、これを焼結させたものを固体電解質に用いることによって高率放電特性に優れるリチウム電池を提案している。しかし、このように酸化物無機固体電解質を用いた全固体リチウム電池においても、従来の非水溶媒を電解液として用いた二次電池と比較して、エネルギー密度、放電電流密度に劣るなどの問題があり、実用化には至っていない。

【0015】無機固体電解質のリチウムイオン伝導度が向上しても、電池としての特性が向上しない原因として、粒子-粒子間の界面抵抗、電極-固体電解質間の界面抵抗が考えられる。材料各自では、十分な特性を有していても、界面抵抗が高いために十分な特性が得られない。

【0016】本発明はこのような従来技術の問題点に鑑みてなされたものであり、電解質のリチウムイオン伝導度が低くて電流密度が小さく、例えばリチウムイオン伝導体である有機溶媒やリチウム塩を含ませる必要があるという従来の問題点を解消したリチウム電池を提供することを目的とする。

【0017】

【課題を解決するための手段】上記目的を達成するために、請求項1に係る発明のリチウム電池では、一対の電極間に固体電解質層を持持してなるリチウム電池であって、前記電極および固体電解質層がシロキサン結合を主骨格とする化合物と非プロトン性溶媒を含んでいることを特徴とする。

【0018】上記リチウム電池では、前記電極が陽極活性物質と固体電解質から成り、前記固体電解質層がこの固体電解質と同一材料から成ることが望ましい。

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【0019】上記リチウム電池では、前記固体電解質層がリチウムイオン伝導性を有する酸化物系結晶化ガラスであることが望ましい。

【0020】上記リチウム電池では、前記非プロトン性溶媒が、アーブチロラクトン、プロピレンカーポネート、エチレンカーポネートのうちのいずれか一種または複数種から成ることが望ましい。

【0021】上記リチウム電池では、前記電極の活物質がLi_{1-x}Mn_{2-x}O₃(0≤x≤0.2), Li₁Mn_{2-x}Me_xO₃(Me=Ni, Cr, Cu, Zn, 0<y≤0.6), Li₁Ti₂O₅、およびLi₁Mn₂O₃のいずれか一種または複数種からなることが望ましい。

【0022】従来の有機系電解液は、非プロトン性溶媒に電解質塩を溶解させることによって電解質にリチウムイオン伝導性を付与するものであるが、本発明では、シロキサン結合を主骨格とする化合物と電解質塩を含まない非プロトン性溶媒を含ませるだけで電池特性が向上するものであり、従来にない伝導機構によってリチウムイオンが移動しているものと思われる。また、シロキサン結合を主骨格とする化合物中に非プロトン性溶媒が存在していることから、液漏れの問題が低減される。

【0023】

【発明の実施の形態】以下、本発明のリチウム電池の実施形態について説明する。

【0024】図1は、本発明に係るリチウム電池の構成例を示す断面図である。図1において、1はパッケージ、2は一対の電極、2aは正極、2bは負極、3は固体電解質層、4は正極集電体、5は負極集電体である。

【0025】パッケージ1は、気密性を保持できれば材質には限定されず、例えばアルミニウム製ラミネート材、ニッケル、アルミニウムなどの金属、あるいはシリコンケースなどを用いることができる。

【0026】正極集電体4または負極集電体5は、正極2aまたは負極2bの集電のために設けられ、例えばアルミニウム(A1)、ニッケル(N1)、銅(Cu)などの金属箔を用いることができる。

【0027】正極2aは、正極活物質粉末からなり、必要に応じて固体電解質層と同一材料の固体電解質粉末が混合される。負極2bは、負極活物質粉末からなり、必要に応じて固体電解質層と同一材料の固体電解質粉末が混合される。正極または負極活物質と固体電解質粉末を混合する場合、電極内のリチウムイオン伝導度の向上が期待されるが、固体電解質粉末の混合量が過多になると、電池の充放電反応に寄与する正極もしくは負極活物質の体積当たりもしくは重量当たりの量が減少し、電池としてのエネルギー密度が低下する。したがって、電極における正極もしくは負極活物質の量は、40重量%以上であることが望ましい。また、この正極2aおよび負極2bには、必要に応じて導電剤が添加される。

【0028】この正極2aおよび負極2bに用いる電極

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活物質としては、例えば、リチウムマンガン複合酸化物、二酸化マンガン、リチウムニッケル複合酸化物、リチウムコバルト複合酸化物、リチウムニッケルコバルト複合酸化物、リチウムバナジウム複合酸化物、リチウムチタン複合酸化物、酸化チタン、酸化ニオブ、酸化バナジウム、酸化タンクス滕などとそれらの誘導体を用いることができる。上述の遷移金属酸化物のうち、特に $L_{1-x}Mn_xO$ ($0 \leq x \leq 0.2$)、 L_iMn_xMeO ($Me = Ni, Cr, Cu, Zn$, $0 < y \leq 0.6$)、 L_iTiO_2 、あるいは $L_iMn_xO_2$ よりなる群は、充放電中の活物質の体積変化が小さい結晶系がスピネル系の活物質であり、良好なサイクル特性を示すものである。ここで、正極活物質と負極活物質には明確な区別ではなく、2種類の化合物の充放電電位を比較して貴な電位を示すものを正極に、卑な電位を示すものを負極にそれぞれ用いて任意の電圧の電池を構成することができる。

【0029】固体電解質層3に用いる固体電解質粉末、正極2aもしくは負極2bに混合する固体電解質粉末としては、 $30L_iI-41L_iO-29P_2O_5$ 、 $40L_iO-35B_2O_5-25L_iNbO_5$ 、 $25L_iO-25Al_2O_3-50SiO_2$ 、 $40L_iO-6Y_2O_3-54SiO_2$ 、あるいは $65L_iNbO_5-35SiO_2$ などの酸化物系非晶質固体電解質や $L_{1-x}M_xT_{1-x}(PO_4)_2$ (ここで M は Al, Sc, Y, La)、 $L_{1-x}Ti_{1-x}(PO_4)_2$ 、 $L_{1-x}R_{1-x}Ti_2O_5$ (ここで R は La, Pr, Nd, Sm)、 $L_{1-x}Al_xT_{1-x}Si_xP_{1-x}O_4$ などの酸化物系結晶化ガラスが挙げられる。固体電解質粉末は、イオン伝導度の観点から、酸化物系結晶化ガラスであることが望ましい。

【0030】導電剤としては、アセチレンブラック、黒鉛、ケッテンブラック、 RuO_2 、 Sb_2O_3 をドープした SnO_2 、あるいは SnO_2 をドープした In_2O_3 などが挙げられる。

【0031】シロキサン結合を形成する化合物としては、シラン化合物が上げられる。シラン化合物では、テトラメトキシシラン、メチルトリメトキシシラン、ジメチルジメトキシシラン、フェニルトリメトキシシラン、ジフェニルジメトキシシラン、テトラエトキシシラン、メチルトリエトキシシラン、ジメチルジエトキシシラン、フェニルトリエトキシシラン、ジフェニルジエトキシシラン、ヘキシルトリメトキシシラン、ポリメトキシロキサン、ポリエトキシロキサン、ポリブトキシロキサンなどが挙げられる。

【0032】電極2(2a, 2b)および固体電解質3の作製方法としては以下の方法が挙げられる。正極、負極活物質粉末、固体電解質粉末と、必要であれば、電子伝導助剤粉末をあらかじめ混合してシラン化合物および非プロトン性溶媒の混合物に分散させる。必要に応じて、イソブロピルアルコール等の溶剤を添加し、スラリ

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一化するとともにスラリー粘度を調整する。このとき固体電解質粉末には電子伝導助剤粉末の混合は不要である。

【0033】また、シラン化合物を硬化させるためには硬化用触媒を用いることもできる。この硬化用触媒は、粉末を分散させる前に添加してもよく、粉末を分散させた後に添加してもよい。

【0034】かくして得られたスラリーは、ドクターブレード法もしくはロールコーナー法などにより、正極集電体4もしくは負極集電体5上に塗布した後にシラン化合物を硬化させる。硬化条件は、硬化用触媒を用いた場合、常温から 150°C ぐらいが適切であり、硬化温度が高いほど保持時間が短くなるが、硬化温度、時間は特に制限されるものではない。また、硬化用触媒を用いない場合、 150°C 以上の温度で加熱することが望ましいが、この場合非プロトン性溶媒の沸点以上の温度は好ましくない。

【0035】ここで、電極2には、必要に応じて固体電解質3と同一の組成である固体電解質を混合させてもよい。

【0036】また、正極2a、負極2b、固体電解質3の積層方法は、正極2a-固体電解質3-負極2bの順に積層した後に一括で加熱硬化させる方法、正極2a、負極2bを別々に成形して、加熱硬化した後にいずれか一方の電極上に固体電解質3を成形し、もう一方の電極を重ねた後に硬化させる方法などが挙げられる。さらに、加熱硬化時に加圧を行なうと紺体の充填率が向上するとともに、電極2-固体電解質3の接合がより強固になって望ましい。

【0037】また、非プロトン性溶媒を含まない全固体電池では、リチウムイオンはパルクでの輸送のみに頼っているが、本発明のリチウム電池では、粒子と粒子表面とを結ぶシロキサン結合を主骨格とする化合物に含まれる非プロトン性溶媒との界面でイオンが移動しているものと推測される。

【0038】本発明が適用されるリチウム電池は、一次電池であっても二次電池であってもよい。電池形状は円筒型、角型、ボタン型、コイン型および扁平型などに限定されるものではない。

【0039】

【実施例】【実施例1】水酸化リチウムと二酸化マンガンを L_i と Mn のモル比が $1:2$ となるように混合し、この混合物を大気中の 900°C で15時間加熱焼成することによってリチウムマンガン複合酸化物(L_iMnO_x)を合成し、これを正極活物質とした。次に、水酸化リチウムと二酸化マンガンを L_i と Mn のモル比が $4:5$ となるように混合し、この混合物を大気中の 600°C で15時間加熱焼成することによってリチウムマンガン複合酸化物($L_iMn_xO_{2-y}$)を合成し、これを負極活物質とした。

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【0040】このLiMn₂O₄に、固体電解質粉末としてLi_{1-x}A_xTi_{1-y}S_yP_{1-z}O_zを体積比で8:2の割合になるように混合し、この混合粉末に対してアセチレンブラックを重量比で90:10の割合になるように混合した。

【0041】シロキサン化合物は以下の手順で準備した。シロキサン化合物（シロキサン化合物濃度：約20wt%，溶剤：約80wt%）に対し、マレイン酸系の硬化用触媒を混合し、常温で攪拌して混合液を作製した。この時、硬化用触媒の混合比は、シロキサン化合物100gに対して120gとした。また、混合液の安定化を図るために、常温で12時間静置した（以下これを調整混合液とする）。

【0042】この調整混合液100gに対してプロピレンカーボネートを5g混合し、良く攪拌した後、前記のLiMn₂O₄とアセチレンブラックの混合粉末を混合してスラリー化した。このスラリーをドクターブレード法でアルミニウム（Al）上に塗付した後に、150°Cの温度で1時間熱処理してシロキサン結合を形成させるとともに電極を得た。

【0043】また、固体電解質粉末Li_{1-x}A_xTi_{1-y}S_yP_{1-z}O_zを前述と同様に調整混合液でプロピレンカーボネートを混合させた液体と混合してスラリー化した。このスラリーをドクターブレード法で前述の正極上に塗付して積層し、150°Cの温度で1時間熱処理することにより、正極2aと固体電解質3の積層体を得た。

【0044】さらに、LiMn₂O₄を正極活性物質であるLiMn₂O₄と同様にスラリー化し、前記の積層体の固体電解質側に塗付積層し、熱処理することによって、正極2a-固体電解質3-負極2bの積層体を得た。得られた積層体の厚みは、約200μmであった。

【0045】得られた積層体の正極2aに正極集電体4を接合すると共に、同様に負極2bに負極集電体5を接合してパッケージ1のアルミニウム製ラミネートに装着した。アルミニウム製ラミネートは35mm×35mmのサイズに切断したものを2枚準備し、前記集電体を接合した積層体を挟み、アルミニウム製ラミネートの外周部を熱圧着することにより、図1に示した35mm×35mmの角型リチウム電池を組み立てた。

【0046】【実施例2】プロピレンカーボネートの変わりにアーピクロラクトンを用いた以外は、正極活性物質および負極活性物質の合成方法、正極2a-固体電解質3-負極2bの成形方法は、実施例1と同様を行った。得られた正極2a-固体電解質3-負極2bの厚みは、約220μmであった。以下、実施例と同様に角型リチウム電池を組み立てた。

【0047】【比較例1】正極活性物質および負極活性物質の合成方法は、実施例1と同様に行った。また、正極-固体電解質-負極の形成方法は、PVdFを結着剤と

し、N-メチル-2-ピロリドンを溶媒として用い、実施例1と同様の手順で行なった。

【0048】得られた正極-固体電解質-負極の厚みは、約180μmであった。さらに積層体の充填率の向上、および粉末の接触面積を向上させる目的でロール加圧を行なった。得られた積層体に対して非プロトン性溶媒の含浸は行なわず、実施例と同様に角型リチウム電池を組み立てた。

（評価）かくして得られた角型固体電解質電池を用いて、充放電装置により、充電条件として50μA/cm²、100μA/cm²、300μA/cm²の電流で前述の角型固体電解質電池に1.5Vまで充電を行い、電圧が1.5Vに到達した後、充電を停止して5分間保持し、その後0.5Vの電圧まで充電時と同じ電流で放電し、次に再度1.5Vまで充電し、この高圧に到達した後、充電を停止して5分間保持する充放電サイクル評価を行った。

【0049】その結果を表1に示す。なお、表中の数字は各放電電流に対する放電容量を示し、単位はmAhである。

【0050】

【表1】

	放電電流 [μA/cm ²]		
	50	100	300
実施例1	21.5	18.8	15.1
実施例2	22.3	17.5	15.8
比較例1	8.6	4.3	-

【0051】表1から、本発明のリチウム電池は、充放電特性に優れていることがわかる。特に放電電流が大きくなってしまって放電容量の低下が小さいことが顯著である。これは、活性物質と固体電解質の空隙にシロキサン結合を主骨格とする化合物と非プロトン性溶媒を介在させることにより、粒子同士の結合と電極と固体電解質の結合が強固になるとともに、パルク内とともに粒子表面と非プロトン性溶媒の界面もリチウムイオン伝導経路となっているものと推測される。

【0052】また、本発明のリチウム電池は、過電圧に對しても安定であり、故意に充放電電圧を上げた場合でも、サイクル特性に影響を及ぼさないことがわかった。これは、非プロトン性溶媒にリチウム塩を含んでいないためであると考えられる。

【0053】さらに、本発明のリチウム電池に含まれる非プロトン性溶媒は、シロキサン結合を主骨格とする化合物内に存在していると考えられ、液漏れはほとんど確認されず、信頼性の高いことも確認された。

【0054】

【発明の効果】以上のように、本発明に係るリチウム電池によれば、電極と固体電解質層がシロキサン結合を主

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 骨格とする化合物と非プロトン性溶媒を含んでいることから、電解質塩を溶解した有機系電解液を用いたリチウム電池と同等の電気化学特性が得られるとともに、従来にないリチウムイオンの伝導機構を示すとともに、電解質塩を含んでいないために、過電圧による電解質塩の分解が起こらない信頼性の高いリチウム電池が得られる。

【図面の簡単な説明】

*

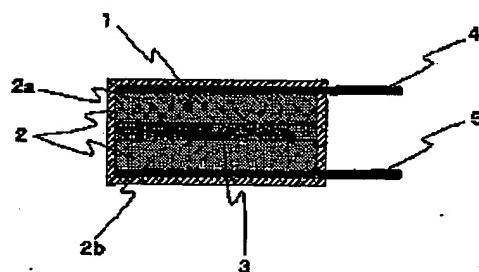
10

* 【図1】本発明に係わるリチウム電池の一実施形態を示す断面図である。

【符号の説明】

1：パッケージ、2：一对の電極、2a：正極、2b：負極、3：固体電解質層、4：正極集電体、5：負極集電体

【図1】



フロントページの続き

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 SH024 AA01 AA02 BB07 CC02 CC03
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 FF15 FF22
 SH029 AJ07 AK02 AK03 AK05 AL02
 AL03 AL04 AM03 AM05 AM11
 AM12 BJ02 BJ03 BJ04 BJ12
 DJ08 DJ09 EJ06 EJ12 HJ02
 SH050 AA13 BA17 CA02 CA05 CA07
 CA08 CA09 CA11 CB02 CB03
 CB05 DA02 DA03 DA09 DA13
 EA13 EA23 HA02

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CLAIMS**[Claim(s)]**

[Claim 1] The lithium cell which is a lithium cell which comes to pinch a solid electrolyte layer to inter-electrode [of a couple], and is characterized by including the compound with which the aforementioned electrode and a solid electrolyte layer make siloxane combination (Si-O) the main skeleton, and the aprotic solvent.

[Claim 2] The lithium cell according to claim 1 characterized by for the aforementioned electrode consisting of an electrode active material and a solid electrolyte, and the aforementioned solid electrolyte layer consisting of the same material as this solid electrolyte.

[Claim 3] The lithium cell according to claim 1 or 2 characterized by the aforementioned solid electrolyte layer consisting of the oxide system glass ceramics which have lithium ion conductivity.

[Claim 4] The claim 1 to which the aforementioned aprotic solvent is characterized by consisting of any one sort of gamma-butyrolactone, propylene carbonate, and ethylene carbonate, or two or more sorts, a lithium cell according to claim 2 or 3.

[Claim 5] The claim 1 to which the active material of the aforementioned electrode is characterized by the bird clapper from any one sort of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 <= x <= 0.2$), $\text{LiMn}_{2-y}\text{MeyO}_4$ (Me=nickel, Zn [Cr, Cu and Zn], $0 < y <= 0.6$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$, or two or more sorts, a claim 2, a lithium cell according to claim 3 or 4.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a lithium cell.

[0002]

[Description of the Prior Art] The energy density of a lithium cell is high, it has little self-discharge, and is widely used for the cellular phone, the notebook computer, etc. taking advantage of the property of being able to respond to a mothball. Generally a cobalt acid lithium (LiCoO₂) and a manganic acid lithium (LiMn₂O₄) are used as a positive active material, and, as for these lithium cells, carbon materials, such as corks and a carbon fiber, are used for the negative-electrode active material.

[0003] Generally, a lithium cell is made into aluminum foil or copper foil with ** with electric conduction agents, such as a positive active material, an above-mentioned negative-electrode active material and above-mentioned acetylene black, and a graphite, and binders, such as a polyvinylidene fluoride (PVdF) and a polytetrafluoroethylene (PTFE), is rolled round in the shape of a spiral through the separator which is the product made from polypropylene, the products made from polyethylene, or those combination, is inserted into a battery-case can, and has structure which it obturated by pouring in the organic system electrolytic solution further.

[0004] The components of these organic system electrolytic solution are an aprotic solvent and an electrolyte salt, as an aprotic solvent, it is used in that propylene carbonate (PC), dimethoxyethane (DME), ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) are independent or the state where it was mixed, and LiClO₄, LiAsF₆, LiBF₄, LiPF₆, LiCF₃SO₃, Li(CF₃SO₂)₂N, etc. are used as an electrolyte salt.

[0005] Moreover, with the thin shape of the various electronic application devices represented by portable information communication terminals, such as a cellular phone and a notebook computer, and the demand of a miniaturization, it replaces with the above organic system electrolytic solutions, and the lithium cell using the polymer electrolyte attracts attention in recent years.

[0006] A polymer electrolyte is the admixture of the macromolecule and electrolyte salt which have the donor type polar group represented by a polyethylene oxide (PEO) and the polypropylene oxide (PPO), an electrolyte layer can be thin-film-ized and improvement in an energy density is expected. Or since there are no worries about a liquid spill and corrosion and an volatile aprotic solvent is not used, that there is little danger of explosion or ignition etc. can desire improvement in a cell property or safety.

[0007] However, the above-mentioned polymer electrolyte has a problem of a low in the degree of ion **** as compared with the organic system electrolytic solution, and since the gel electrolyte which mixed the organic system electrolytic solution to the polymer electrolyte has the ionic conductivity which is equal to the organic system electrolytic solution, development is performed briskly.

[0008] When such a gel electrolyte is used, it is difficult to keep ideal electric contact of a solid electrolyte layer and an electrode layer. in JP,7-326383,A Carry out the laminating of what the solvent was mixed [what] with the electrolyte salt to the high molecular compound, and carried out the polymerization of the monomer constituent to it to a positive-active-material layer, and some monomer constituents are infiltrated into a positive-active-material layer. Fully sticking a positive-

active-material layer and a solid polymer electrolyte is proposed by carrying out the polymerization of the monomer constituent which carried out the laminating on the front face of the monomer constituent and positive active material into which the positive-active-material layer was infiltrated, sticking to a positive-active-material layer, and producing a solid polymer electrolyte in the laminating state.

[0009] Moreover, in JP,8-111233,A, reducing resistance of the interface of the positive electrode and solid electrolyte in which the ends or the end of a principal chain of a polyether, the poly thioether, or a polyacrylate carried out the chemical bond to the positive-electrode oxide front face, and the interfacial resistance of positive-active-material particles is proposed.

[0010] Moreover, in JP,8-315855,A, by inserting the mixture of the organic compound, the organic solvent, and lithium salt which have the functional group in which a polymerization is possible between two electrodes, and completing a polymerization after that, generation of the interface between an electrolyte and an electrode is prevented and preventing ablation with a solid electrolyte and an electrode etc. is proposed.

[0011] Moreover, in JP,9-50816,A, while excelling in a mechanical property or processability by distributing metal carbonation objects, such as Li₂CO₃, and CoCO₃, NiCO₃, MgCO₃, in the polyelectrolyte which mixed the electrolyte salt with the solute, the high compound solid electrolyte of the chemical stability in an interface with a negative electrode is proposed.

[0012] However, by these methods, still, there is a problem to which current density becomes small low, and electrolytic lithium ion conductivity needed to include many the organic solvents and lithium salt which are a main lithium ion conductor. Moreover, by including lithium salt in an organic solvent, there is a problem to which the withstand voltage to electrochemical reaction becomes low, and there is a problem of being unstable, to an overvoltage.

[0013] Furthermore, development of the solid electrolyte cell which used the inorganic compound for the solid electrolyte is also furthered. There are no generating of the DIN drama id and defluxion of an active material, and excelling in a charge-and-discharge cycle life is proposed. [in / a negative electrode / with all the solid-state lithium cells that make a positive electrode the compound which consists of a transition-metals oxide and a transition-metals sulfide as a positive active material, and use the glass solid electrolyte of lithium ion conductivity and lithium containing Li₂S, and the metal to alloy as a negative electrode] However, since this proposal contains the compound of a sulfide system in a positive electrode and a solid electrolyte, it has problems, such as being rich in reactivity with moisture.

[0014] Moreover, in the lithium ion conductor of an oxide system, there is crystalline-substance glass which has the same crystal structure as a NASICON system, and the lithium cell which is excellent in a high-rate-discharge property is proposed by using for a solid electrolyte the thing which made this sinter. However, in all the solid-state lithium cells that used the oxide inorganic solid electrolyte in this way, as compared with the rechargeable battery using the conventional non-aqueous solvent as the electrolytic solution, there are problems, such as being inferior to an energy density and discharge current density, and it has not resulted in utilization.

[0015] Even if the lithium ion conductivity of an inorganic solid electrolyte improves, the interfacial resistance between particle-particles and the interfacial resistance between electrode-solid electrolytes can be considered as a cause whose property as a cell does not improve. Even if it has property sufficient with the material in each, since the interfacial resistance is high, sufficient property is not acquired.

[0016] this invention is made in view of the trouble of such conventional technology, and it aims at offering the lithium cell which canceled the conventional trouble that electrolytic lithium ion conductivity needed to be low, and current density needed to be small, for example, it was necessary to include the organic solvent and lithium salt which are a lithium ion conductor.

[0017]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, in the lithium cell of invention concerning a claim 1, it is the lithium cell which comes to pinch a solid electrolyte layer to inter-electrode [of a couple], and is characterized by including the compound with which the aforementioned electrode and a solid electrolyte layer make siloxane combination the main skeleton,

and the aprotic solvent.

[0018] It is desirable for the aforementioned electrode to consist of an electrode active material and a solid electrolyte, and for the aforementioned solid electrolyte layer to consist of the same material as this solid electrolyte in the above-mentioned lithium cell.

[0019] It is desirable for the aforementioned solid electrolyte layers to be the oxide system glass ceramics which have lithium ion conductivity in the above-mentioned lithium cell.

[0020] It is desirable for the aforementioned aprotic solvent to consist of any one sort in gamma-butyrolactone, propylene carbonate, and ethylene carbonate or two or more sorts in the above-mentioned lithium cell.

[0021] In the above-mentioned lithium cell, any one sort or two or more sorts to the bird clapper of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.2$), $\text{LiMn}_{2-y}\text{MeyO}_4$ (Me=nickel, Zn [Cr, Cu and Zn], $0 < y \leq 0.6$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ has the desirable active material of the aforementioned electrode.

[0022] Although the conventional organic system electrolytic solution gives lithium ion conductivity to an electrolyte by dissolving an electrolyte salt in an aprotic solvent, in this invention, a cell property improves only by including the compound which makes siloxane combination the main skeleton, and the aprotic solvent which does not contain an electrolyte salt, and it is thought that the lithium ion is moving according to the conduction mechanism which is not in the former. Moreover, since the aprotic solvent exists in the compound which makes siloxane combination the main skeleton, the problem of a liquid spill is reduced.

[0023]

[Embodiments of the Invention] Hereafter, the operation gestalt of the lithium cell of this invention is explained.

[0024] Drawing 1 is the cross section showing the example of composition of the lithium cell concerning this invention. drawing 1 -- setting -- 1 -- for a positive electrode and 2b, as for a solid electrolyte layer and 4, a negative electrode and 3 are [a package and 2 / the electrode of a couple, and 2a / a positive-electrode charge collector and 5] negative-electrode charge collectors

[0025] If airtightness can be held, a package 1 is not limited to the quality of the material, for example, can use metals, such as lamination material made from aluminum, nickel, and aluminum, or a shrink case.

[0026] The positive-electrode charge collector 4 or the negative-electrode charge collector 5 is formed in the current collection sake of positive-electrode 2a or negative-electrode 2b, for example, metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), can be used for it.

[0027] Positive-electrode 2a consists of the end of positive-active-material complications, and the solid electrolyte powder of the same material as a solid electrolyte layer is mixed if needed. Negative-electrode 2b consists of negative-electrode active material powder, and the solid electrolyte complications end of the same material as a solid electrolyte layer is mixed if needed. Although improvement in the lithium ion conductivity in an electrode is expected when mixing solid electrolyte powder with a positive electrode or a negative-electrode active material, if the amount of mixtures of solid electrolyte powder becomes excessive, per volume of the positive electrode which contributes to the charge-and-discharge reaction of a cell, or a negative-electrode active material, or the amount per weight will decrease, and the energy density as a cell will fall. Therefore, as for the amount of the positive electrode in an electrode, or a negative-electrode active material, it is desirable that it is 40 % of the weight or more. Moreover, an electric conduction agent is added by this positive-electrode 2a and negative-electrode 2b if needed.

[0028] As an electrode active material used for this positive-electrode 2a and negative-electrode 2b, a lithium manganese multiple oxide, manganese dioxide, a lithium nickel multiple oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, a niobium oxide, a vanadium oxide, tungstic oxides, etc. and those derivatives can be used, for example. Among above-mentioned transition-metals oxides, crystal system with the small volume change of the active material in charge and discharge is the active material of a spinel system, and especially the group that consists of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.2$), $\text{LiMn}_{2-y}\text{MeyO}_4$ (Me=nickel, Zn [Cr, Cu and Zn], $0 < y \leq 0.6$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, or $\text{Li}_4\text{Mn}_5\text{O}_{12}$ shows a good cycle property. Here, what shows **** potential to a positive electrode for what

a clear distinction does not have in a positive active material and a negative-electrode active material, compares the charge and discharge potential of two kinds of compounds, and shows electropositive potential can be used for a negative electrode, respectively, and the cell of arbitrary voltage can be constituted.

[0029] As solid electrolyte powder mixed to the solid electrolyte powder used for the solid electrolyte layer 3, positive-electrode 2a, or negative-electrode 2b 30LiI-41Li₂O-29P₂O₅, Oxide system noncrystalline-solid electrolytes and Li_{1+x}M_xTi(s) 2-x, such as 40Li(s)O-35B-20S-25LiNbO₃, 25Li₂O-25aluminum₂O₃-50SiO₂, 40Li₂O-6Y₂O₃-54SiO₂, or 65LiNbO₂-35SiO₂ (PO₄)₃ (M is aluminum, Sc, Y, and La here), Li_{1+x}Ti_{2-x}(PO₄)₃, Li_{0.5-3x}R_{0.5+x}TiO₃ (it La(s) R here) Oxide system glass ceramics, such as Pr, Nd, Sm, and Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂, are mentioned. As for solid electrolyte powder, it is desirable that they are the oxide system glass ceramics from a viewpoint of ionic conductivity.

[0030] As an electric conduction agent, acetylene black, a graphite, KETCHIEN black, SnO₂ that doped RuO₂ and Sb 2O₃, or In 2O₃ which doped SnO₂ is mentioned.

[0031] A silane compound is raised as a compound which forms siloxane combination. With a silane compound, a tetramethoxy silane, methyl trimetoxysilane, dimethyl dimethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, a tetrapod ethoxy silane, methyl triethoxysilane, dimethyl diethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, hexyl trimethoxysilane, the poly methoxy siloxane, a poly ethoxy siloxane, a poly butoxy siloxane, etc. are mentioned.

[0032] The following methods are mentioned as the production method of an electrode 2 (2a; 2b) and a solid electrolyte 3. If required, electronic-conduction assistant powder will be beforehand mixed with a positive electrode, negative-electrode active material powder, and solid electrolyte powder, and a silane compound and the mixture of an aprotic solvent are distributed. Slurry viscosity is adjusted while adding and slurring solvents, such as isopropyl alcohol, if needed. At this time, mixture of electronic-conduction assistant powder is unnecessary to solid electrolyte powder.

[0033] Moreover, in order to stiffen a silane compound, the catalyst for hardening can also be used. It may add, before distributing powder, and after distributing powder, you may add this catalyst for hardening.

[0034] By the doctor blade method or the roll-coater method, after applying the slurry obtained in this way on the positive-electrode charge collector 4 or the negative-electrode charge collector 5, it stiffens a silane compound. When the catalyst for hardening is used for hardening conditions, although the holding time becomes short so that about 150 degrees C is suitable from ordinary temperature and a curing temperature is high, a curing temperature and especially time are not restricted. Moreover, although it is desirable to heat at the temperature of 150 degrees C or more when not using the catalyst for hardening, the temperature more than the boiling point of an aprotic solvent is not desirable in this case.

[0035] You may make an electrode 2 mix the solid electrolyte which is the same composition as a solid electrolyte 3 here if needed.

[0036] Moreover, after it fabricates separately the method of carrying out heat hardening by package after carrying out a laminating to the order of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b, positive-electrode 2a, and negative-electrode 2b and positive-electrode 2a, negative-electrode 2b, and the laminating method of a solid electrolyte 3 carry out heat hardening, they fabricate a solid electrolyte 3 on one of electrodes, and the method of stiffening, after piling up another electrode etc. is mentioned. Furthermore, if it pressurizes at the time of heat hardening, while the filling factor of **** will improve, junction of the electrode 2-solid electrolyte 3 becomes firmer and is desirable.

[0037] Moreover, at all the solid state batteries that do not contain an aprotic solvent, although it depends for the lithium ion only on transportation by bulk, with the lithium cell of this invention, it is guessed that it is what ion is moving by the interface with the aprotic solvent contained in the compound which makes the main frame siloxane combination which wets a particle and a particle front face.

[0038] Even if the lithium cell with which this invention is applied is a primary cell, it may be a rechargeable battery. A cell configuration is not limited to cylindrical, a square shape, a button type, a

coin type, a flat type, etc.

[0039]

[Example] A [example 1] lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 1:2, by carrying out heating baking of this mixture at 900 degrees C in the atmosphere for 15 hours, the lithium manganese multiple oxide (LiMn₂O₄) was compounded, and this was made into the positive active material. Next, a lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 4:5, by carrying out heating baking of this mixture at 600 degrees C in the atmosphere for 15 hours, the lithium manganese multiple oxide (Li₄Mn₅O₁₂) was compounded, and this was made into the negative-electrode active material.

[0040] As solid electrolyte powder, to this LiMn₂O₄, Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂ was mixed so that it might become the rate of 8:2 by the volume ratio, and to this end of mixed powder, to it, acetylene black was mixed so that it might become the rate of 90:10 by the weight ratio.

[0041] The siloxane compound was prepared in the following procedures. To the siloxane compound (siloxane compound concentration : about 20 wt(s)%, a solvent : about 80 wt(s)%), the catalyst for hardening of a maleic-acid system was mixed, it stirred in ordinary temperature, and mixed liquor was produced. At this time, the mixing ratio of the catalyst for hardening was set to 120g to 100g of siloxane compounds. Moreover, in order to attain stabilization of mixed liquor, it put in ordinary temperature for 12 hours (let this be adjustment mixed liquor below).

[0042] After mixing 5g and stirring propylene carbonate well to 100g of this adjustment mixed liquor, the mixed-powder end of above LiMn₂O₄ and acetylene black was mixed and slurred. The electrode was obtained, while heat-treating at the temperature of 150 degrees C for 1 hour and making siloxane combination form, after carrying out this slurry with ** on aluminum (aluminum) by the doctor blade method.

[0043] Moreover, it mixed with the liquid with which adjustment mixed liquor was made to mix propylene carbonate like the above-mentioned, and end Li of solid electrolyte complications Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂ was slurred. The layered product of positive-electrode 2a and a solid electrolyte 3 was obtained by carrying out this slurry with **, carrying out a laminating on the above-mentioned positive electrode, by the doctor blade method, and heat-treating at the temperature of 150 degrees C for 1 hour.

[0044] Furthermore, Li₄Mn₅O₁₂ was slurred like LiMn₂O₄ which is a positive active material, the laminating with ** was carried out to the solid electrolyte side of the aforementioned layered product, and the layered product of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was obtained by heat-treating. The thickness of the obtained layered product was about 200 micrometers.

[0045] While joining the positive-electrode charge collector 4 to positive-electrode 2a of the obtained layered product, the negative-electrode charge collector 5 was similarly joined to negative-electrode 2b, and the lamination made from aluminum of a package 1 was equipped. The lamination made from aluminum assembled the 35mmx35mm square shape lithium cell shown in drawing 1 by preparing two things cut in 35mmx35mm size, inserting the layered product which joined the aforementioned charge collector, and carrying out thermocompression bonding of the periphery section of the lamination made from aluminum.

[0046] The forming method of the synthetic method of a positive active material and a negative-electrode active material and positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was performed like the example 1 except having used gamma-butyrolactone for the change of [example 2] propylene carbonate. The thickness of obtained positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was about 220 micrometers. Hereafter, the square shape lithium cell was assembled like the example.

[0047] The synthetic method of the [example 1 of comparison] positive active material and a negative-electrode active material was performed like the example 1. Moreover, the formation method of a positive-electrode-solid electrolyte-negative electrode made PVdF the binder, and performed it in the same procedure as an example 1, using a N-methyl-2-pyrrolidone as a solvent.

[0048] The thickness of the obtained positive-electrode-solid electrolyte-negative electrode was about 180 micrometers. Roll pressurization was performed in order to raise the improvement in the filling

factor of a layered product, and a powdered touch area furthermore. It did not perform sinking [of an aprotic solvent] in to the obtained layered product, but the square shape lithium cell was assembled like the example.

The square shape solid electrolyte cell obtained in this way is used. (Evaluation) With a charging and discharging device It charges to 1.5V with the current of

50microA/cm²,100microA/cm²,300microA/cm² as charge conditions at the above-mentioned square shape solid electrolyte cell. After suspended charge, holding for 5 minutes, discharging with the current same to the voltage of after that 0.5V as the time of charge, charging to 1.5V again next, after voltage reached 1.5V, and reaching this voltage, charge-and-discharge cycle evaluation which suspends charge and is held for 5 minutes was performed.

[0049] The result is shown in Table 1. In addition, the number of front Naka shows the service capacity to each discharge current, and a unit is mAh.

[0050]

[Table 1]

	放電電流 [μ A / cm ²]		
	5 0	1 0 0	3 0 0
実施例 1	21. 5	18. 8	15. 1
実施例 2	22. 3	17. 5	15. 8
比較例 1	6. 6	4. 3	-

[0051] Table 1 shows that the lithium cell of this invention is excellent in a charge-and-discharge property. Even if especially the discharge current becomes large, it is remarkable that the fall of service capacity is small. It is guessed that this is that from which the particle front face and the interface of an aprotic solvent have also been a lithium ion conduction path with the inside of bulk while combination of combination and the electrode of particles, and a solid electrolyte becomes firm by making the compound and aprotic solvent which make siloxane combination the main skeleton placed between the openings of an active material and a solid electrolyte.

[0052] Moreover, the lithium cell of this invention was stable also to the overvoltage, and even when charge and discharge voltage is raised intentionally, it turns out that a cycle property is not affected. This is considered to be because for lithium salt not to be included in an aprotic solvent.

[0053] Furthermore, it was thought that the aprotic solvent contained in the lithium cell of this invention existed in the compound which makes siloxane combination the main skeleton, and most liquid spills were not checked, but it was checked that it is also reliable.

[0054]

[Effect of the Invention] As mentioned above, since the electrolyte salt is not included while the conduction mechanism of the lithium ion which is not in the former while an electrochemistry property equivalent to the lithium cell using the organic system electrolytic solution which dissolved the electrolyte salt is acquired according to the lithium cell concerning this invention, since the electrode and the solid electrolyte layer contain the compound and aprotic solvent which make siloxane combination the main skeleton is shown, a lithium cell with the high reliability from which disassembly of the electrolyte salt by the overvoltage does not take place is obtained.

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a lithium cell.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, it is while according to the lithium cell concerning this invention an electrochemistry property equivalent to the lithium cell using the organic system electrolytic solution which dissolved the electrolyte salt is acquired since the electrode and the solid electrolyte layer contain the compound and aprotic solvent which make siloxane combination the main frame. Since the electrolyte salt is not included while the conduction mechanism of the lithium ion which is not in the former is shown, a lithium cell with the high reliability from which disassembly of the electrolyte salt by the overvoltage does not take place is obtained.

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TECHNICAL PROBLEM

[Description of the Prior Art] The energy density of a lithium cell is high, it has little self-discharge, and is widely used for the cellular phone, the notebook computer, etc. taking advantage of the property of being able to respond to a mothball. Generally a cobalt acid lithium (LiCoO₂) and a manganic acid lithium (LiMn₂O₄) are used as a positive active material, and, as for these lithium cells, carbon materials, such as corks and a carbon fiber, are used for the negative-electrode active material.

[0003] Generally a lithium cell is electric conduction agents, such as a positive active material, an above-mentioned negative-electrode active material and above-mentioned acetylene black, and a graphite, and binders, such as a polyvinylidene fluoride (PVdF) and a polytetrafluoroethylene (PTFE). It is made with ** aluminum foil or copper foil, and it is rolled round in the shape of a spiral through the separator which is the product made from polypropylene, the products made from polyethylene, or those combination, is inserted into a battery-case can, and has structure which it obturated by pouring in the organic system electrolytic solution further.

[0004] The components of these organic system electrolytic solution are an aprotic solvent and an electrolyte salt. As an aprotic solvent, propylene carbonate (PC), dimethoxyethane (DME), ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) are used in independent or the state where it was mixed, and LiClO₄, LiAsF₆, LiBF₄, LiPF₆, LiCF₃SO₃, Li(CF₃SO₂)₂N, etc. are used as an electrolyte salt.

[0005] Moreover, with the thin shape of the various electronic application devices represented by portable information communication terminals, such as a cellular phone and a notebook computer, and the demand of a miniaturization, it replaces with the above organic system electrolytic solutions, and the lithium cell using the polymer electrolyte attracts attention in recent years.

[0006] A polymer electrolyte is the admixture of the macromolecule and electrolyte salt which have the donor type polar group represented by a polyethylene oxide (PEO) and the polypropylene oxide (PPO), an electrolyte layer can be thin-film-ized and improvement in an energy density is expected. Or since there are no worries about a liquid spill and corrosion and an volatile aprotic solvent is not used, that there is little danger of explosion or ignition etc. can desire improvement in a cell property or safety.

[0007] However, the above-mentioned polymer electrolyte has the problem that the degree of ion *** is low as compared with the organic system electrolytic solution, and since the gel electrolyte which mixed the organic system electrolytic solution to the polymer electrolyte has the ionic conductivity which is equal to the organic system electrolytic solution, development is performed briskly.

[0008] It is difficult to keep ideal electric contact of a solid electrolyte layer and an electrode layer, when such a gel electrolyte is used, for example, it is at JP,7-326383,A. Carry out the laminating of what the solvent was mixed [what] with the electrolyte salt to the high molecular compound, and carried out the polymerization of the monomer constituent to it to a positive-active-material layer, and some monomer constituents are infiltrated into a positive-active-material layer. Fully sticking a positive-active-material layer and a solid polymer electrolyte is proposed by carrying out the polymerization of the monomer constituent which carried out the laminating on the front face of the monomer constituent and positive active material into which the positive-active-material layer was infiltrated, sticking to a positive-active-material layer, and producing a solid polymer electrolyte in

the laminating state.

[0009] Moreover, in JP,8-111233,A, reducing resistance of the interface of the positive electrode and solid electrolyte in which the ends or the end of a principal chain of a polyether, the poly thioether, or a polyacrylate carried out the chemical bond to the positive-electrode oxide front face, and the interfacial resistance of positive-active-material particles is proposed.

[0010] Moreover, in JP,8-315855,A, by inserting the mixture of the organic compound, the organic solvent, and lithium salt which have the functional group in which a polymerization is possible between two electrodes, and completing a polymerization after that, generation of the interface between an electrolyte and an electrode is prevented and preventing exfoliation with a solid electrolyte and an electrode etc. is proposed.

[0011] Moreover, in JP,9-50816,A, while excelling in a mechanical property or processability by distributing metal carbonation objects, such as Li₂CO₃, and CoCO₃, NiCO₃, MgCO₃, in the polyelectrolyte which mixed the electrolyte salt with the solute, the high compound solid electrolyte of the chemical stability in an interface with a negative electrode is proposed.

[0012] However, by these methods, still, there is a problem to which current density becomes small low, and electrolytic lithium ion conductivity needed to include many the organic solvents and lithium salt which are a main lithium ion conductor. Moreover, by including lithium salt in an organic solvent, there is a problem to which the withstand voltage to electrochemical reaction becomes low, and there is a problem of being unstable, to an overvoltage.

[0013] Furthermore, development of the solid electrolyte cell which used the inorganic compound for the solid electrolyte is also furthered. There are no generating of DIN DORAIDO and omission of an active material, and excelling in a charge-and-discharge cycle life is proposed. [in / a negative electrode / with all the solid-state lithium cells that make a positive electrode the compound which consists of a transition-metals oxide and a transition-metals sulfide as a positive active material, and use the glass solid electrolyte of lithium ion conductivity and lithium containing Li₂S, and the metal to alloy as a negative electrode] However, since this proposal contains the compound of a sulfide system in a positive electrode and a solid electrolyte, it has problems, such as being rich in reactivity with moisture.

[0014] Moreover, in the lithium ion conductor of an oxide system, there is crystalline-substance glass which has the same crystal structure as a NASICON system, and the lithium cell which is excellent in a high-rate-discharge property is proposed by using for a solid electrolyte the thing which made this sinter. However, in all the solid-state lithium cells that used the oxide inorganic solid electrolyte in this way, as compared with the rechargeable battery using the conventional non-aqueous solvent as the electrolytic solution, there are problems, such as being inferior to an energy density and discharge current density, and it has not resulted in utilization.

[0015] Even if the lithium ion conductivity of an inorganic solid electrolyte improves, the interfacial resistance between particle-particles and the interfacial resistance between electrode-solid electrolytes can be considered as a cause whose property as a cell does not improve. Even if it has property sufficient with the material in each, since the interfacial resistance is high, sufficient property is not acquired.

[0016] this invention is made in view of the trouble of such conventional technology, and it aims at offering the lithium cell which canceled the conventional trouble that electrolytic lithium ion conductivity needed to be low, and current density needed to be small, for example, it was necessary to include the organic solvent and lithium salt which are a lithium ion conductor.

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, in the lithium cell of invention concerning a claim 1, it is the lithium cell which comes to pinch a solid electrolyte layer to inter-electrode [of a couple], and is characterized by including the compound with which the aforementioned electrode and a solid electrolyte layer make siloxane combination the main skeleton, and the aprotic solvent.

[0018] It is desirable for the aforementioned electrode to consist of an electrode active material and a solid electrolyte, and for the aforementioned solid electrolyte layer to consist of the same material as this solid electrolyte in the above-mentioned lithium cell.

[0019] It is desirable for the aforementioned solid electrolyte layers to be the oxide system glass ceramics which have lithium ion conductivity in the above-mentioned lithium cell.

[0020] It is desirable for the aforementioned aprotic solvent to consist of any one sort in gamma-butyrolactone, propylene carbonate, and ethylene carbonate or two or more sorts in the above-mentioned lithium cell.

[0021] In the above-mentioned lithium cell, any one sort or two or more sorts to the bird clapper of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.2$), $\text{LiMn}_{2-y}\text{MeyO}_4$ (Me=nickel, Zn [Cr, Cu and Zn], $0 < y \leq 0.6$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and $\text{Li}_4\text{Mn}'_5\text{O}_{12}$ has the desirable active material of the aforementioned electrode.

[0022] Although the conventional organic system electrolytic solution gives lithium ion conductivity to an electrolyte by dissolving an electrolyte salt in an aprotic solvent, in this invention, a cell property improves only by including the compound which makes siloxane combination the main skeleton, and the aprotic solvent which does not contain an electrolyte salt, and it is thought that the lithium ion is moving according to the conduction mechanism which is not in the former. Moreover, since the aprotic solvent exists in the compound which makes siloxane combination the main skeleton, the problem of a liquid spill is reduced.

[0023]

[Embodiments of the Invention] Hereafter, the operation gestalt of the lithium cell of this invention is explained.

[0024] Drawing 1 is the cross section showing the example of composition of the lithium cell concerning this invention. drawing 1 -- setting -- 1 -- for a positive electrode and 2b, as for a solid electrolyte layer and 4, a negative electrode and 3 are [a package and 2 / the electrode of a couple, and 2a / a positive-electrode charge collector and 5] negative-electrode charge collectors

[0025] If airtightness can be held, a package 1 is not limited to the quality of the material, for example, can use metals, such as lamination material made from aluminum, nickel, and aluminum, or a shrink case.

[0026] The positive-electrode charge collector 4 or the negative-electrode charge collector 5 is formed in the current collection sake of positive-electrode 2a or negative-electrode 2b, for example, metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), can be used for it.

[0027] Positive-electrode 2a consists of the end of positive-active-material complications, and the solid electrolyte powder of the same material as a solid electrolyte layer is mixed if needed. Negative-electrode 2b consists of negative-electrode active material powder, and the solid electrolyte complications end of the same material as a solid electrolyte layer is mixed if needed. Although improvement in the lithium ion conductivity in an electrode is expected when mixing solid electrolyte powder with a positive electrode or a negative-electrode active material, if the amount of mixtures of

solid electrolyte powder becomes excessive, per volume of the positive electrode which contributes to the charge-and-discharge reaction of a cell, or a negative-electrode active material, or the amount per weight will decrease, and the energy density as a cell will fall. Therefore, as for the amount of the positive electrode in an electrode, or a negative-electrode active material, it is desirable that it is 40 % of the weight or more. Moreover, an electric conduction agent is added by this positive-electrode 2a and negative-electrode 2b if needed.

[0028] As an electrode active material used for this positive-electrode 2a and negative-electrode 2b, a lithium manganese multiple oxide, manganese dioxide, a lithium nickel multiple oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, a niobium oxide, a vanadium oxide, tungstic oxides, etc. and those derivatives can be used, for example. Among above-mentioned transition-metals oxides, crystal system with the small volume change of the active material in charge and discharge is the active material of a spinel system, and especially the group that consists of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.2$), $\text{LiMn}_{2-y}\text{Me}_y\text{O}_4$ ($\text{Me} = \text{nickel, Zn [Cr, Cu and Zn], } 0 < y \leq 0.6$), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, or $\text{Li}_4\text{Mn}_5\text{O}_{12}$ shows a good cycle property. Here, what shows **** potential to a positive electrode for what a clear distinction does not have in a positive active material and a negative-electrode active material, compares the charge and discharge potential of two kinds of compounds, and shows electropositive potential can be used for a negative electrode, respectively, and the cell of arbitrary voltage can be constituted.

[0029] As solid electrolyte powder mixed to the solid electrolyte powder used for the solid electrolyte layer 3, positive-electrode 2a, or negative-electrode 2b $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$, Oxide system noncrystalline-solid electrolytes and $\text{Li}_{1+x}\text{MxTi(s)}_{2-x}$, such as $40\text{Li(s)O}-35\text{B}-2\text{O}_5-25\text{LiNbO}_3$, $25\text{Li}_2\text{O}-25\text{aluminum2O}_3-50\text{SiO}_2$, $40\text{Li}_2\text{O}-6\text{Y2O}_3-54\text{SiO}_2$, or $65\text{LiNbO}_2-35\text{SiO}_2$ (PO_4)₃ (M is aluminum, Sc, Y, and La here), $\text{Li}_{1+x}\text{Ti}_{2-x}(\text{PO}_4)_3$, $\text{Li}_{0.5-3x}\text{R}_{0.5+x}\text{TiO}_3$ (it La(s) R here) Oxide system glass ceramics, such as Pr, Nd, Sm, and $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_3-y\text{O}_{12}$, are mentioned. As for solid electrolyte powder, it is desirable that they are the oxide system glass ceramics from a viewpoint of ionic conductivity.

[0030] As an electric conduction agent, acetylene black, a graphite, KETCHIEN black, SnO_2 that doped RuO_2 and Sb 2O_3 , or In 2O_3 which doped SnO_2 is mentioned.

[0031] A silane compound is raised as a compound which forms siloxane combination. With a silane compound, a tetramethoxy silane, methyl trimetoxysilane, dimethyl dimethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, a tetrapod ethoxy silane, methyl triethoxysilane, dimethyl diethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, hexyl trimethoxysilane, the poly methoxy siloxane, a poly ethoxy siloxane, a poly butoxy siloxane, etc. are mentioned.

[0032] The following methods are mentioned as the production method of an electrode 2 (2a, 2b) and a solid electrolyte 3. If required, electronic-conduction assistant powder will be beforehand mixed with a positive electrode, negative-electrode active material powder, and solid electrolyte powder, and a silane compound and the mixture of an aprotic solvent are distributed. Slurry viscosity is adjusted while adding and slurring solvents, such as isopropyl alcohol, if needed. At this time, mixture of electronic-conduction assistant powder is unnecessary to solid electrolyte powder.

[0033] Moreover, in order to stiffen a silane compound, the catalyst for hardening can also be used. It may add, before distributing powder, and after distributing powder, you may add this catalyst for hardening.

[0034] By the doctor blade method or the roll-coater method, after applying the slurry obtained in this way on the positive-electrode charge collector 4 or the negative-electrode charge collector 5, it stiffens a silane compound. When the catalyst for hardening is used for hardening conditions, although the holding time becomes short so that about 150 degrees C is suitable from ordinary temperature and a curing temperature is high, a curing temperature and especially time are not restricted. Moreover, although it is desirable to heat at the temperature of 150 degrees C or more when not using the catalyst for hardening, the temperature more than the boiling point of an aprotic solvent is not desirable in this case.

[0035] You may make an electrode 2 mix the solid electrolyte which is the same composition as a solid electrolyte 3 here if needed.

[0036] Moreover, after it fabricates separately the method of carrying out heat hardening by package after carrying out a laminating to the order of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b, positive-electrode 2a, and negative-electrode 2b and positive-electrode 2a, negative-electrode 2b, and the laminating method of a solid electrolyte 3 carry out heat hardening, they fabricate a solid electrolyte 3 on one of electrodes, and the method of stiffening, after piling up another electrode etc. is mentioned. Furthermore, if it pressurizes at the time of heat hardening, while the filling factor of *** will improve, junction of the electrode 2-solid electrolyte 3 becomes firmer and is desirable.

[0037] Moreover, at all the solid state batteries that do not contain an aprotic solvent, although it depends for the lithium ion only on transportation by bulk, with the lithium cell of this invention, it is guessed that it is what ion is moving by the interface with the aprotic solvent contained in the compound which makes the main skeleton siloxane combination which wets a particle and a particle front face.

[0038] Even if the lithium cell with which this invention is applied is a primary cell, it may be a rechargeable battery. A cell configuration is not limited to cylindrical, a square shape, a button type, a coin type, a flat type, etc.

[Translation done.]

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EXAMPLE

[Example] A [example 1] lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 1:2, by carrying out heating baking of this mixture at 900 degrees C in the atmosphere for 15 hours, the lithium manganese multiple oxide (LiMn_2O_4) was compounded, and this was made into the positive active material. Next, a lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 4:5, by carrying out heating baking of this mixture at 600 degrees C in the atmosphere for 15 hours, the lithium manganese multiple oxide ($\text{Li}_4\text{Mn}_5\text{O}_{12}$) was compounded, and this was made into the negative-electrode active material.

[0040] As solid electrolyte powder, to this LiMn_2O_4 , $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ was mixed so that it might become the rate of 8:2 by the volume ratio, and to this end of mixed powder, to it, acetylene black was mixed so that it might become the rate of 90:10 by the weight ratio.

[0041] The siloxane compound was prepared in the following procedures. To the siloxane compound (siloxane compound concentration : about 20 wt(s)%, a solvent : about 80 wt(s)%), the catalyst for hardening of a maleic-acid system was mixed, it stirred in ordinary temperature, and mixed liquor was produced. At this time, the mixing ratio of the catalyst for hardening was set to 120g to 100g of siloxane compounds. Moreover, in order to attain stabilization of mixed liquor, it put in ordinary temperature for 12 hours (let this be adjustment mixed liquor below).

[0042] After mixing 5g and stirring propylene carbonate well to 100g of this adjustment mixed liquor, the mixed-powder end of above LiMn_2O_4 and acetylene black was mixed and slurred. The electrode was obtained, while heat-treating at the temperature of 150 degrees C for 1 hour and making siloxane combination form, after carrying out this slurry with ** on aluminum (aluminum) by the doctor blade method.

[0043] Moreover, it mixed with the liquid with which adjustment mixed liquor was made to mix propylene carbonate like the above-mentioned, and end $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ was slurred. The layered product of positive-electrode 2a and a solid electrolyte 3 was obtained by carrying out this slurry with **, carrying out a laminating on the above-mentioned positive electrode, by the doctor blade method, and heat-treating at the temperature of 150 degrees C for 1 hour.

[0044] Furthermore, $\text{Li}_4\text{Mn}_5\text{O}_{12}$ was slurred like LiMn_2O_4 which is a positive active material, the laminating with ** was carried out to the solid electrolyte side of the aforementioned layered product, and the layered product of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was obtained by heat-treating. The thickness of the obtained layered product was about 200 micrometers.

[0045] While joining the positive-electrode charge collector 4 to positive-electrode 2a of the obtained layered product, the negative-electrode charge collector 5 was similarly joined to negative-electrode 2b, and the lamination made from aluminum of a package 1 was equipped. The lamination made from aluminum assembled the 35mmx35mm square shape lithium cell shown in drawing 1 by preparing two things cut in 35mmx35mm size, inserting the layered product which joined the aforementioned charge collector, and carrying out thermocompression bonding of the periphery section of the lamination made from aluminum.

[0046] The forming method of the synthetic method of a positive active material and a negative-electrode active material and positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was performed like the example 1 except having used gamma-butyrolactone for the change of [example 2]

propylene carbonate. The thickness of obtained positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was about 220 micrometers. Hereafter, the square shape lithium cell was assembled like the example.

[0047] The synthetic method of the [example 1 of comparison] positive active material and a negative-electrode active material was performed like the example 1. Moreover, the formation method of a positive-electrode-solid electrolyte-negative electrode made PVdF the binder, and performed it in the same procedure as an example 1, using a N-methyl-2-pyrrolidone as a solvent.

[0048] The thickness of the obtained positive-electrode-solid electrolyte-negative electrode was about 180 micrometers. Roll pressurization was performed in order to raise the improvement in the filling factor of a layered product, and a powdered touch area furthermore. It did not perform sinking [of an aprotic solvent] in to the obtained layered product, but the square shape lithium cell was assembled like the example.

The square shape solid electrolyte cell obtained in this way is used. (Evaluation) With a charging and discharging device It charges to 1.5V with the current of

50microA/cm², 100microA/cm², 300microA/cm² as charge conditions at the above-mentioned square shape solid electrolyte cell. After suspended charge, holding for 5 minutes, discharging with the current same to the voltage of after that 0.5V as the time of charge, charging to 1.5V again next, after voltage reached 1.5V, and reaching this voltage, charge-and-discharge cycle evaluation which suspends charge and is held for 5 minutes was performed.

[0049] The result is shown in Table 1. In addition, the number of front Naka shows the service capacity to each discharge current, and a unit is mAh.

[0050]

[Table 1]

	放電電流 [μA/cm ²]		
	50	100	300
実施例 1	21.5	18.8	15.1
実施例 2	22.3	17.5	15.8
比較例 1	6.6	4.3	—

[0051] Table 1 shows that the lithium cell of this invention is excellent in a charge-and-discharge property. Even if especially the discharge current becomes large, it is remarkable that the fall of service capacity is small. It is guessed that this is that from which the particle front face and the interface of an aprotic solvent have also been a lithium ion conduction path with the inside of bulk while combination of combination and the electrode of particles, and a solid electrolyte becomes firm by making the compound and aprotic solvent which make siloxane combination the main skeleton placed between the openings of an active material and a solid electrolyte.

[0052] Moreover, the lithium cell of this invention was stable also to the overvoltage, and even when charge and discharge voltage is raised intentionally, it turns out that a cycle property is not affected. This is considered to be because for lithium salt not to be included in an aprotic solvent.

[0053] Furthermore, it was thought that the aprotic solvent contained in the lithium cell of this invention existed in the compound which makes siloxane combination the main skeleton, and most liquid spills were not checked, but it was checked that it is also reliable.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the cross section showing 1 operation gestalt of the lithium cell concerning this invention.

[Description of Notations]

1: A package, the electrode of 2:couple, a 2a:positive electrode, a 2b:negative electrode, 3:solid electrolyte layer, 4:positive-electrode charge collector, 5 : negative-electrode charge collector

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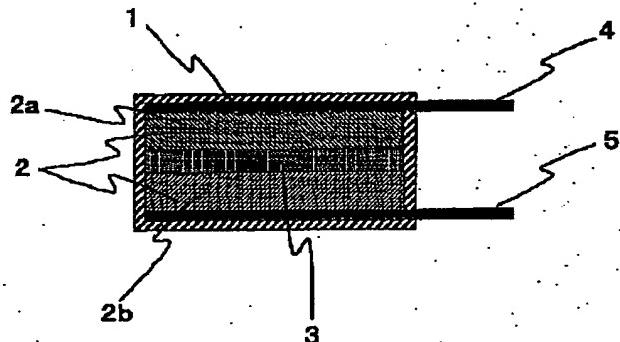
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DRAWINGS

[Drawing 1]



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